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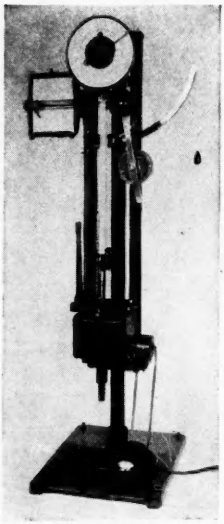

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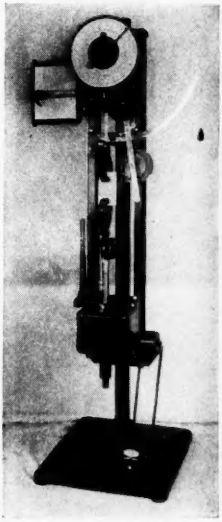

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The Rôle of Cystine in the Structure of the Fibrous Protein, Wool

By W. I. PATTERSON, W. B. GEIGER, L. R. MIZELL and M. HARRIS

A Textile Foundation Publication

Abstract

Wool is remarkable among textile materials in that it possesses high extensibility and the ability to return to its original length or shape after being stretched or distorted. These properties are of advantage in such products as clothing, blankets, and carpets. It is shown that a number of the important physical properties as well as some of the chemical properties of wool are dependent upon a unique molecular structure, provided by the presence of disulfide or cystine cross-linkages between the main molecular chains of the fiber. As a result, wool fibers possess a three-dimensional molecular net-work while most other textile fibers are composed of bundles of chain-like molecules, arranged more or less parallel to the axes of the fibers.

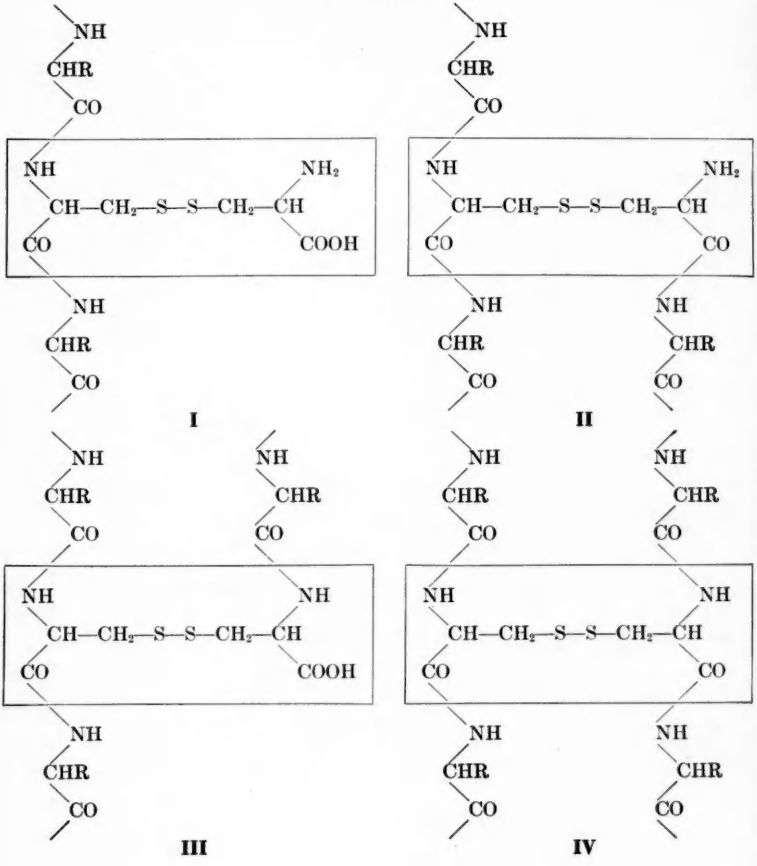
The rôle of these disulfide cross-linkages is made clear by a study of the behavior of wool before and after alteration of the mode of linkage of the sulfur. For example, the disulfide cross-linkages are readily broken to form sulfhydryl groups by the reducing agent, thioglycolic acid. The sulfhydryl groups of the reduced fibers readily react with alkyl halides to form thioether groups with two possible results. Thus, the reaction of reduced wool with alkyl monohalides results in permanent rupture of disulfide linkages and greatly increases the extensibility and decreases the strength of the fibers. The reaction with aliphatic dihalides introduces hydrocarbon chains between pairs of sulfur atoms of cystine molecules in the fibers. Such fibers are very similar to untreated fibers in physical properties.

Wools in which the disulfide linkages have been broken by reduction, or by reduction followed by treatment with alkyl monohalides possesses much higher alkali-solubilities than untreated wool, while wools in which the disulfide cross-linkages have been replaced by new cross-linkages through reduction followed by reaction with dihalides possess much lower alkali-solubilities. Since the susceptibility of wool to degradation by alkalies is one of its greatest disadvantages, practical processes that would make it stable at its cross-linkages should also enhance its durability.

I. Introduction

PROTEINS, according to the hypothesis of Hofmeister[1] and Fischer,[2] consist of amino acids joined through amide (peptide) linkages to form long chain structures called polypeptides. On the basis of this hypothesis, many of the similarities among proteins should be due to the large number of peptide linkages, while dissimilarities among them should be related to variations in the proportions and arrangement of the constituent amino acids, to differences in the lengths and arrangement of the polypeptide chains, and to the presence of linkages other than peptide.

Formulae



The present paper is concerned with the relationship of one such linkage, the disulfide linkage of the amino acid cystine, to the properties of the fibrous protein, wool.

Although cystine contains two amino and two carboxyl groups, it appears that all of these groups are involved in peptide links in most, if not all, of the cystine residues. If the cystine of wool were combined in a peptide chain only through amino and carboxyl groups attached to the same carbon atom (Formula I), processes that break disulfide bonds should result in the elimination from the wool of one-half of the sulfur. This possibility is not supported by experiment, since reduced wool contains as much sulfur as the original material. Were either (or both) or the amino groups of cystine uncombined (Formula II), treatment of wool with nitrous acid would destroy at least half of the cystine in the former case and all of it in the latter. The investigations of Hess and Sullivan,[3] as well as unpublished work in this laboratory, show that only a small portion is destroyed by this reagent. Evidence derived from titrations[4, 5] indicates that no considerable number of carboxyl groups of cystine in wool can be free (Formula III) since the number of free carboxyl groups is essentially accounted for by the content of glutamic and aspartic acids. While these data do not afford complete proof, they strongly indicate that all the functional groups of all the cystine are combined, and that only a small proportion, if any, can be free.

On the basis of these considerations at least the major portion of the cystine must form parts of either two separate polypeptide chains (Formula IV) or of a single folded polypeptide chain, and in either case its disulfide group would serve as a connecting or a cross link. Astbury and Street[6] were the first to suggest that such disulfide cross linkages were present in wool protein; since then Astbury, and Speakman, with their collaborators, have extended this hypothesis.

This view suggests that modification of the mode of linkage of the sulfur in wool should lead to profound alterations in the properties of the fiber. Unfortunately, since many of the processes known to affect disulfide linkages, such as the action of light, of alkalies, and of oxidizing and of some reducing agents, involve side reactions with other groups in the protein, conclusions based on their use may be open to criticism. The action of a few reducing agents, however, appears to be solely with the disulfide groups and therefore it appeared possible to use these reagents in evaluating the relation of the disulfide groups to the structure and properties of the wool fiber. Of these reagents, only thioglycolic acid and certain other mercaptans can reduce each disulfide group to two sulfhydryl groups. Other reagents, such as potassium cyanide, sodium sulfide and sodium bisulfite react with disulfide groups to form not only sulfhydryl groups but others as well.[7]

Goddard and Michaelis[7, 8] found that strongly alkaline solutions of thioglycolic acid rapidly converted the disulfide groups of wool to sulfhydryl groups, and that under these conditions, rapid dissolution of the wool occurred. These authors used alkaline solutions since they observed that wool was not dissolved by neutral or acid solutions of the reagent, an observation that led them to conclude that wool could be reduced only at a pH of 10 or higher. Such a conclusion is not compatible with the behavior of disulfides in general, which are known to be readily reduced over a wide range of pH values. In the present investigation, it is shown that the

disulfide groups of wool can also be reduced by thioglycolic acid over a wide range of pH, and that if the reduction is carried out in neutral or acid solutions, the fibrous structure of the wool is not destroyed. The use of neutral or faintly acidic solutions of the reducing agent also has the advantage of eliminating such secondary reactions as degradation of cystine, cysteine, peptide, or other linkages.

Wool that has been reduced in neutral or acid solution can be further modified without loss of fibrous structure by treatment with alkyl halides, which convert the sulfhydryl groups to thioether groups.* The reactions may be represented as follows:

(1) $W—S—S—W + 2HS—CH_2—COOH \rightarrow 2W—SH + (S—CH_2—COOH_2$
(2) $W—SH + RX \rightarrow W—SR + HX$

where W represents the portions of the wool connected by the disulfide groups, R represents an alkyl group, and X, a halogen atom. Reactions of this type result in the permanent rupture of covalent cross-linkages. Wool fibers have been prepared in which the mode of linkage of at least 95 per cent of the cystine has been modified through these reactions.

Dihalides are also capable of reacting with the reduced wool, the reaction being represented by the following equation:

(3) $2W—SH + (CH_2)_nX \rightarrow W—S—(CH_2)_n—S—W + 2HX$

The reaction with the dihalides results in the formation of new cross links † in which sulfur atoms of the cystine are connected by short hydrocarbon chains.

The reactions in eq 2 and 3 offered a means of preparing a large number of wool derivatives. Thus, it was possible not only to investigate the nature of the sulfur linkages and their relation to the structure of the fiber but also to study the effects of introducing into the fiber new groups having widely different properties.

II. Experimental Procedure

1. Materials

The wool fibers used in the present study were part of the lot used in earlier investigations reported from this laboratory.[12] This material had been subjected to no mechanical or chemical treatment other than successive extractions with alcohol and with ether at room temperature for 5 hours each, followed by washing with water at 40° C.

Worsted yarn was also used for some experiments. It was prepared from raw wool that had been previously extracted with Stoddard solvent and washed with water. The yarn was further purified by extraction in a Soxhlet apparatus with alcohol and with ether for 6 hours each, and finally washed with distilled water.

* Goddard and Michaelis, [7, 8] and Pillemer, Ecker and Wells [9, 10] also found that their amorphous wool protein derivative could be alkylated by treatment with alkyl monohalides to form other amorphous protein derivatives.

† Speakman [11] has suggested that divalent metal ions, such as that of barium, can form cross-linkages between sulfur atoms. Such linkages would be ionic and unstable, as compared with completely homopolar linkages formed according to eq 1 and 3.

2. Methods

a. Reduction of wool with thioglycolic acid

Aqueous solutions of thioglycolic acid were used, and were adjusted to the desired pH by adding potassium hydroxide solution. The final concentration of thioglycolic acid in the solution was determined by titration with standard iodine solution.[13] It was found advisable to cool the thioglycolic acid solution in an ice bath during addition of the potassium hydroxide, since at higher temperatures the solutions often became colored. Although aqueous solutions of thioglycolic acid were used in all experiments reported in this paper, solutions of the reagent in organic solvents were also found effective.

The reduction was carried out by immersing a known weight of wool in a solution of thioglycolic acid at the required temperature, pH, and concentration. Wetting the wool was facilitated by evacuating the vessel with a filter pump. After the reduction had been allowed to proceed for the desired length of time, the wool was removed and washed several times with distilled water to remove excess thioglycolic acid and its oxidation products.

b. Reoxidation of sulfydryl groups of reduced wool

Before the reduced wool was reoxidized it was first washed thoroughly with 95-per cent ethyl alcohol. Omission of this step led to products that contained amounts of sulfur in excess of that in the untreated wool, presumaby by the formation of a mixed disulfide, one-half derived from cystine, the other half from thioglycolic acid. The wool was then rinsed with distilled water, placed in 0.1 *M* potassium phosphate buffer solution at pH 7.0, and a stream of oxygen bubbled through the solution until the wool no longer gave a positive nitroprusside reaction.[14] Finally the wool was again washed with distilled water, and dried in a stream of air.

c. Alkylation of the sulfhydryl groups of reduced wool

Reduced wool that was to be alkylated was transferred immediately after washing to a 1.0 *M* phosphate buffer solution at pH 8.0, in which had been dissolved or suspended the desired alkylating agent. The rate of alkylation was increased by agitation of the mixture, particularly when the alkylating agent was not completely soluble. Ordinarily, 0.002 mole of alkylating agent and 100 ml of buffer solution were used for each gram of wool. The reaction was allowed to proceed until a negative nitroprusside test for sulfhydryl groups in the fiber was obtained.

The reactions take place not only in aqueous buffer solutions but also in organic solvents in the presence of soluble or insoluble substances capable of removing the acid formed in the reaction. For example, solutions of reagents in 50-per cent aqueous methanol, 0.05 *M* with respect to NH_4OH and 0.1 M with respect to NH_4Cl, or in benzene in the presence of sodium bicarbonate, were found to be satisfactory.

d. Analytical methods

The extent to which the sulfhydryl groups of the reduced wool had been alkylated was determined by analyzing the wool for cystine by the Sullivan [15] procedure, as previously used in this laboratory.[16] Neither thio-

glycolic acid nor thioethers derived from cystine affect the color reaction of the cystine under these conditions. The adequacy of this method of determining the amount of reaction was checked in certain cases by alkylating the reduced wool with *p*-chlorobenzyl chloride, a reagent that introduces an atom of halogen for each sulfhydryl group with which it reacts. For example, one product that contained 2.2 per cent of chlorine (0.00063 equivalent per gram), also was found to contain 4.7 per cent of cystine. The original wool contained 12.4 per cent of cystine, so allowing for the increase in weight due to introduction of *p*-chlorobenzyl groups during the reaction, the product contained a calculated total of 11.4 per cent of reacted plus unreacted cystine. By subtracting the 4.7 per cent of unreacted cystine from this total, it is seen that 6.7 per cent or 0.00056 equivalent of cystine in each gram of wool had reacted. The amount of halogen introduced therefore corresponds, within analytical error, with the decrease in cystine content of the wool.

The amount of halogen was determined by the Pregl bead-tube method.[17] Sulfur determinations were made by the oxygen-bomb method.[18]

The hygroscopicity * of the wool was determined by keeping air-dried samples in a room at 21° C. and 65-per cent relative humidity for 24 hours, and determining the loss in weight on drying in a vacuum oven at 105° C. for 2 hrs. The values are calculated as percentages of the dry weights.

Alkali solubility was measured by the method of Harris and Smith.[19] Samples were treated with 0.1 *N* sodium hydroxide solution for 1 hour at 65° C., and the percentage loss in weight was determined.

e. Determination of physical properties of the wool

Two tests were utilized in determining the changes produced in the physical properties of the fiber during the various treatments. The first involved the measurement of the breaking strength of treated yarn by the single-strand method on a pendulum-type machine. The values reported are the averages of 10 or more determinations.

In the second test, the stress-strain characteristics of individual fibers were determined, by the method described by Sookne and Harris.[12] This method, which is a modification of procedures used by other investigators,† is much more sensitive to small changes and has greater accuracy than methods involving a determination of the breaking strengths. It is based upon the observation of Speakman [5] that when a wool fiber is immersed in water and stretched under load until it has been elongated 30 per cent, it will return practically to its original length when the load is removed. If the fiber is allowed to relax in the unstretched state in water for about 24 hours, and then again stretched exactly as before, it is found that the same amount of energy (within about 1 per cent) is required to stretch the fiber the second time. If the fiber after the first stretching is subjected to chemical treatments which break chemical bonds, less energy will be required to stretch it the second time. The ratio of the energy required to stretch the fiber the second time to that required the first time is called the *30-per cent index*. It follows that if the 30-per cent index is less than 1, the fiber has been weakened by the treatment; if it is greater than 1,

* Hygroscopicity is used here in an arbitrary way. Actually, the amount of moisture absorbed by wool will vary both with temperature and relative humidity.

† For literature citations see [12].

strengthened. The accuracy of this method depends on the fact that comparisons are always made between successive measurements on the *same* fiber. Since wool fibers are extremely irregular and vary considerably in shape and cross-section, comparisons between different fibers would give rise to larger errors, which could be only partially eliminated by the application of statistical methods to measurements on large numbers of fibers. With the present technique, as few as 3 fibers were found sufficient to provide adequate checks.

III. Results and Discussion

1. The Course of the Reduction Reaction

The reaction of wool with thioglycolic acid under a variety of conditions was investigated, and is described in the following sections.

a. Effect of pH

Preliminary work showed that solutions of thioglycolic acid to which no alkali had been added reacted with wool, and resulted in the production of sulfhydryl groups, which gave a positive nitroprusside reaction, and were capable of reacting with alkyl halides. These reactions proceeded without destruction of the fiber, whereas strongly alkaline solutions (pH 11.0

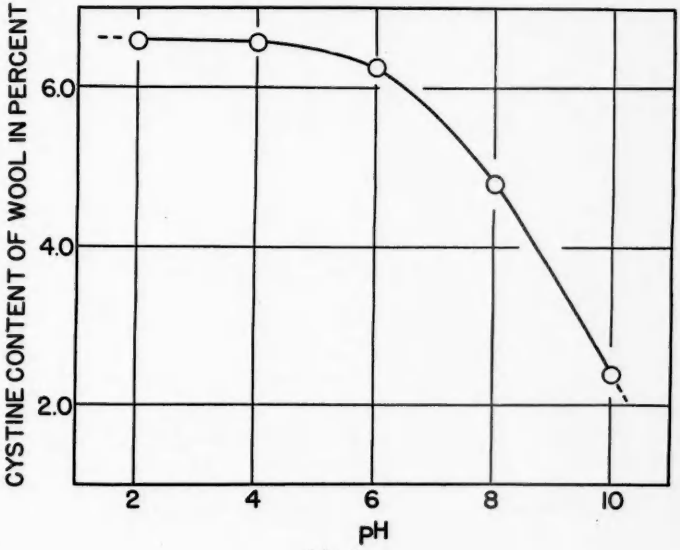


Fig. 1.

Cystine content of wool after reduction at various pH values for 20 hours at 35° C. with 0.2 *M* thioglycolate solutions, and alkylation with *p*-chlorobenzyl chloride.

or above) of the reagent reacted with the wool, not only to reduce it, but also to dissolve it.[7, 8] The effect of various pH values was studied in greater detail by reducing several samples of wool with a 0.2 *M* solution of thioglycolic acid solutions at 35° C. for 20 hours at various pH values, then alkylating with p-chlorobenzyl chloride, and finally determining the amount of unchanged cystine. The results are shown in figure 1. It will be noted that the amount of reduction was practically constant over the pH range of 2 to 6, somewhat greater at pH 8, and very markedly greater at pH 10. The decrease in cystine in the alkaline region is due not to destruction of cystine by alkali but to reduction, since wool that has been reduced for short periods (2 hrs.) under these conditions can be reoxidized to products containing nearly the original amounts of cystine and sulfur. Longer exposure (20 hrs.) of wool to thioglycolic acid at pH 10 resulted in material that contains an abnormally low amount of cystine after reoxidation, but because a considerable portion of the wool was dissolved under such conditions, the results were probably caused by extraction of cysteine-rich material. The increased reduction in alkaline solutions may be caused by ionization of sulfhydryl groups. This could change the mechanism of action of the reducing agent, and also, ionization of sulfhydryl groups formed in the wool itself would increase swelling and facilitate penetration of the reagent.

Wool reduced in acid solution maintained its original appearance, but wool reduced at pH values of 9.0 or above became gelatinous when wet, and brittle and resinous when dry.

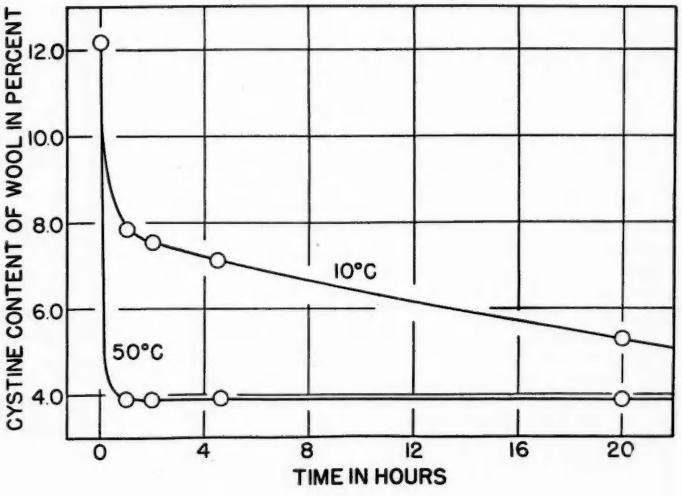


Fig. 2.

Cystine content of wool after reduction for various lengths of time at pH 4.5 and 35° C. with 0.2 *M* thioglycolate, and alkylation with *p*-chlorobenzyl chloride.

b. Effect of the duration of the treatment

The amount of cystine reduced during treatment of wool for various lengths of time with 0.2 *M* thioglycolic acid at pH 4.5 and 35° C. is shown in figure 2. Under these conditions the reaction proceeded to about one-half of its final extent in the first 2 hours, and to about 95 per cent of its final extent in 8 hours.

c. Effect of the concentration of thioglycolic acid

The amount of cystine reduced in 20 hrs. at 35° C. and at pH 4.5 by various concentrations of thioglycolic acid is indicated in figure 3. Sufficient reducing reagents to insure the presence of at least 20 times the

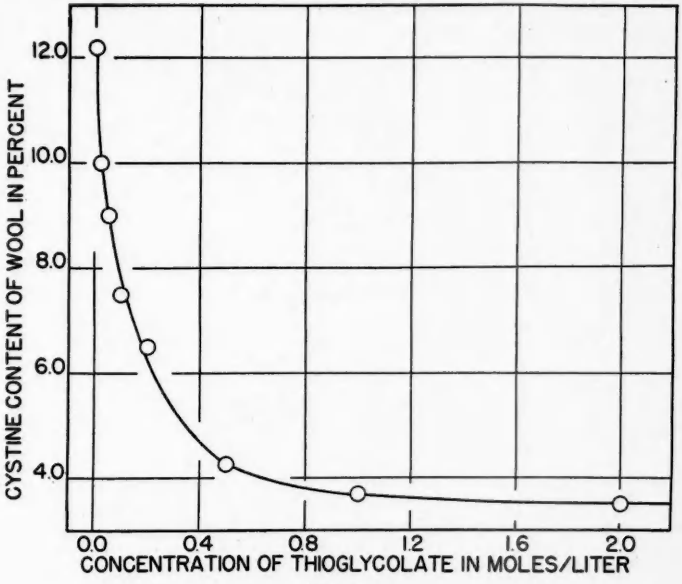


Fig. 3.

Cystine content of wool after reduction with thioglycolate solutions of various concentrations for 20 hours at pH 4.5 and 35° C., and alkylation with *p*-chlorobenzyl chloride.

amount of thioglycolic acid theoretically necessary to reduce all the disulfide groups of the wool was used in each experiment. The amount of reduction increased rapidly in the range 0.01 *M* to 0.2 *M*. The effect was less marked between 0.2 *M* and 0.5 *M*, while increasing the concentration of thioglycolic acid beyond 0.5 *M* had little further effect.

d. Effect of temperature

The amounts of cystine reduced during treatment of wool for various lengths of time with 1.0 *M* thioglycolic acid at pH 4.5 and at 10° C. and

50° C. are shown in figure 4. At 50° C., the reaction was essentially complete after 1 hour, while at 10° the reaction proceeded more slowly. Increasing the temperature, however, did not increase markedly the amount of cystine finally reduced.

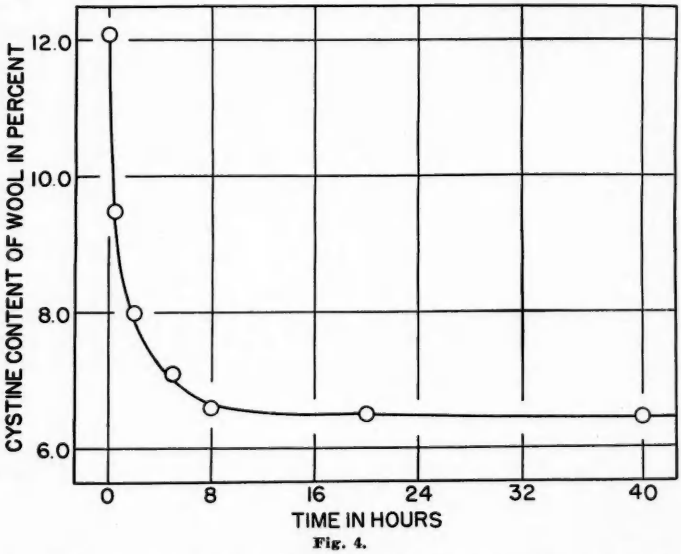


Fig. 4.

Cystine content of wool after reduction with 1.0 *M* thioglycolate at 10° C. and at 50° C. at pH 4.5 or various lengths of time, and alkylation with *p*-chlorobenzyl chloride.

2. Alkylation

Most of the alkyl halides that were investigated were found to react more or less readily with reduced wool. In general, the reaction took from 6 to 24 hours at 35° C. to reach completion, depending on the amount of reduction of the wool and on the reagent used. It was found that iodides reacted faster than bromides, and bromides faster than chlorides. Tertiary alkyl halides, such as tertiary butyl chloride, and triphenylmethyl chloride, were found to be almost completely unreactive.

Besides the reagents listed in table 1, the following were also found to be reactive: allyl chloride, 2-methylallyl chloride, chloroacetone, methyl chloromethyl ether, ethyl chloride, ethylene dichloride, ethylene oxide, epichlorohydrin, 1, 3-dichloroisopropanol and 1, 3-dibromisopropanol.

3. The Properties of Reduced and Alkylated Wools

The properties of wool fibers and yarn that had been modified by reduction and alkylation are summarized in the following sections. In each instance, the wool was reduced for 20 hours at 35° C. and pH 4.5 with a large excess of 0.2 *M* thioglycolate. Duplicate experiments were found to lead to variations amounting to less than 0.02 in the 30-per cent indices, 0.3 per cent in hydrations, and 0.5 per cent in alkali-solubilities. Analyses

Table 1. 30-percent indices and breaking strengths of wools reduced and alkylated with alkyl monohalides.

Treatment	30-percent index	Breaking strength
		grams
Untreated	0.99	1310
Reduction	0.65	1170
Reduction and reoxidation	0.97	1310
Reduction and CH_3I	0.67	1190
Reduction and C_2H_5Br	0.70	1250
Reduction and $C_6H_5CH_2Cl$	0.92	1310
Reduction and p-$ClC_6H_4CH_2Cl$	0.95	1450
Reduction and $C_7H_{15}Br$	0.95	1380
Reduction and $C_{12}H_{25}Br$	0.96	1340
Reduction and $ClCH_2COOH$	0.67	1240

showed that the materials contained 6.5 ± 0.5 per cent of cystine in every case; that is, the mode of linkage of approximately half of the sulfur atoms had been altered; since the untreatd wool contained 12.4 per cent of cystine.

(a) Physical properties

As indicated by table 1, the breaking of cross-linkages during reduction greatly decreased the 30-per cent index of the fibers. Reduction followed by reoxidation resulted in the restoration of nearly the original 30-per cent index, indicating practically complete reaction of the sulfhydryl groups to rebuild disulfide cross-linkages. Fibers modified by reduction followed by alkylation with an alkyl monohalide of low molecular weight, such as methyl iodide or ethyl bromide, were only slightly less easily elongated than those reduced alone. Alkylation with chloroacetic acid introduced ionizable carboxyl groups (combined as —S—CH_2COOH) into the fiber. The data show that wool fibers treated in this manner have 30-per cent indices of the same order as those of wool fibers reduced alone.

Reduction of wool followed by alkylation with monohalides of higher molecular weight, such as benzyl chloride, p chlorobenzyl chloride, heptyl bromide, or dodecyl bromide gave products higher in 30-per cent index than those obtained with methyl iodide or ethyl bromide. Such behavior appears to be due either to the action of intermolecular forces of the van der Waals type between alkyl groups on neighboring sulfur atoms, or between these groups and other parts of the polypeptide chains of the protein. Such secondary linkages would be expected to be weaker than the original covalent type. The data in table 1 offer support for such a hypothesis.

When aliphatic dihalides are used to alkylate reduced wool, groupings that may be represented as W—S—$(CH_2)_n$—S—W appear to replace the disulfide bridges of the original wool, as eq. 3 indicates. Analogous reactions of dihalides with simple mercaptans are known,[20] and evidence that the reaction proceeds in this way is found both in the properties of the products, and in the fact that they are practically free of halogen. The halogen contents of several samples of wool prepared by reduction and alkylation with trimethylene dibromide are shown in table 2. Included in the table are halogen contents calculated on the basis of the assumption that only one of the bromine atoms of the dihalide had reacted. It is readily seen that only a very small fraction of the dihalide molecules had

Table 2. Bromine content of wool reduced and alkylated with trimethylene dibromide.

Calculated results are based on the assumption that only one bromine atom of each dihalide molecule has reacted.

Cystine reacted	Bromine calculated	Bromine found
percent	percent	percent
2.1	1.6	0.1
6.4	5.0	0.1
8.4	6.5	0.0
10.2	7.9	0.2

reacted in this way. Extensibility of the wool prepared in this way would be expected to be slightly increased, presumably since the cross-linkages between polypeptide chains would be lengthened, and it should increase further as the number of methylene groups separating the two sulfur atoms is increased. The data obtained with fibers reduced and treated with methylene iodide, ethylene dibromide, trimethylene dibromide, and tetramethylene dibromide show such a trend (table 3).

Table 3. 30-percent indices and breaking strengths of wools reduced and alkylated with alkyl dihalides.

Treatment	30-percent index	Breaking strength
		grams
Untreated	0.99	1310
Reduction and CH_2I_2	0.94	1380
Reduction and $(CH_2)_2Br_2$	0.92	1420
Reduction and $(CH_2)_3Br_2$	0.90	1460
Reduction and $(CH_2)_4Br_2$	0.88	1380

The breaking strengths of yarn treated like the fibers show similar trends (tables 1 and 3). Reduced wool, reduced and methylated wool, and wool reduced and treated with chloroacetic acid were markedly lower in breaking strength than the untreated wool, while wool that had been reduced and alkylated with monohalides of high molecular weight, or with a dihalide, was not far different from untreated wool in this respect.

b. Hygroscopicity

The hygroscopicity of the modified wools varied depending on the chemical nature of the groups introduced into the wool, as shown in tables 4 and 5. Wools into which large groups have been introduced by alkylation with benzyl chloride, *p*-chlorobenzyl chloride, heptyl bromide, or dodecyl bromide were found to be less hygroscopic than untreated wool. By introducing hydrophobic groups of high molecular weight into the wool the percentage of hydrophilic structures, such as peptide bonds, is decreased, and as a result the products are less highly hydrated.

The introduction of small groups by alkylation with methyl iodide, ethyl bromide, or an alkyl dihalide of low molecular weight should lead to introduction of only a small percentage of hydrophobic groups. As would be expected, these products were found to be very little different from untreated wool in hygroscopicity. The introduction of a polar group, as

Table 4. Alkali-solubility and hygroscopicity of wools reduced and alkylated with monohalides.

Treatment	Alkali-solubility	Moisture content
	percent	percent
Untreated	10.5	16.0
Reduction	ca. 50.0	—
Reduction and reoxidation	12.5	16.3
Reduction and CH_3I	33.0	16.3
Reduction and C_2H_5Br	18.3	16.2
Reduction and $C_6H_5CH_2Cl$	15.4	14.8
Reduction and *p*-$ClC_6H_4CH_2Cl$	12.8	14.0
Reduction and $C_7H_{15}Br$	18.0	15.6
Reduction and $C_{12}H_{25}Br$	18.2	15.6
Reduction and $ClCH_2COOH$	ca. 50.0	16.9

Table 5. Alkali-solubility and hygroscopicity of wools reduced and alkylated with dihalides.

Treatment	Alkali-solubility	Moisture content
	percent	percent
Untreated	10.5	16.0
Reduction and CH_2I_2	5.2	16.4
Reduction and $(CH_2)_2Br_2$	6.6	16.2
Reduction and $(CH_2)_3Br_2$	5.3	16.0
Reduction and $(CH_2)_4Br_2$	7.0	16.3

by reduction and alkylation with chloroacetic acid, yielded products that were somewhat more hygroscopic than untreated wool.

(*c*) *Alkali solubility*

Reduction of wool, followed by alkylation with an alkyl monohalide may be expected to render the wool more readily soluble in alkali, since this process breaks disulfide bonds which form links between polypeptide chains, and therefore decreases the average molecular weight of the wool proteins. The high alkali-solubilities of wool that has been reduced and treated with alkyl monohalides illustrates such a behavior. The extremely high alkali-solubility of wool alkylated with methyl iodide may be due to the formation of sulfonium groupings according to the following equation:

$$WSCH_3 + CH_3I \rightarrow W - S(CH_3)_2^+ + I^-$$

Methyl iodide is known to be exceptionally reactive in this respect.[21] Sulfonium compounds are highly ionized and would be expected to increase the alkali-solubility.

Reduction breaks disulfide cross-linkages, a process which lowers the molecular weight and at the same time introduces ionizable sulfhydryl groups into the wool. Each of these changes should tend to increase the solubility of the wool in alkali, and observations confirmed this expectation. In view of these results, it is apparent why strongly alkaline solutions of thioglycolic acid, as observed by Goddard and Michaelis,[7, 8] are capable of

dissolving wool. Reduction followed by alkylation with chloroacetic acid should also yield products that possess high alkali-solubility, since carboxyl groups also are ionized in alkaline solution. Such wool was found to be very readily dissolved by alkali.

Reduction of wool, followed by treatment with polymethylene dihalides such as methylene iodide, ethylene dibromide, trimethylene dibromide or tetramethylene dibromide, maintains the original molecular weight of the protein, and also replaced disulfide cross-linkages, which are unstable toward alkali,[22] with stable bis-thioether * cross-linkages as eq. 3 indicates. Such a process was found greatly to increase the resistance of wool to the action of alkali. The alkali-solubilities (table 5) of these samples were much lower than those of untreated wool, or of any of the wools reduced and then alkylated with alkyl monohalides.

(d) Effect of Varying the Extent of Reduction and Alkylation

The results described in the preceeding sections were obtained from wool that had been reduced to nearly the same cystine content and then alkylated. The relation between the extent of reduction and alkylation, as judged from the decrease in content of unchanged cystine and the properties of the products, has also been studied, using two of the alkylating agents, methyl iodide and trimethylene dibromide. The experimental results are summarized in table 6.

It is apparent that in both cases the 30-per cent index decreased as the extent of reduction and alkylation increased. Fibers that had been reduced and methylated, however, were decidedly more changed in this respect than those which had been reduced and treated with trimethylene dibromide. The breaking strengths of yarn treated along with the fibers show the same trend as the 30-per cent indices, but are a considerably less sensitive measure of the changes that have taken place.

Table 6. Properties of wool reduced to indicated cystine content and alkylated with indicated reagents.

Cystine	30-percent index	Breaking strength	Alkali solubility
percent		grams	percent
A. Untreated			
12.2	0.99	1310	10.5
B. Alkylated with $(CH_2)_3Br_2$			
10.3	0.99	1338	5.8
6.0	0.86	1318	3.7
4.0	0.72	1272	2.6
2.2	0.68	1012	2.5
C. Alkylated with CH_3I			
10.3	0.73	1287	13.2
6.0	0.48	1250	31.5
4.0	0.27	1240	43.5
2.2	0.18	989	83.0

* This terminology is in accord with the suggestions of Patterson and Curran.[23]

Of particular interest is the fact that, while the alkali-solubility of the reduced and methylated wool increased as its content of unchanged cystine decreased, that of the wool reduced and treated with trimethylene dibromide decreased. This contrasting behavior furnishes further evidence that reduction followed by methylation breaks disufide cross-linkages and decreases the average molecular weight of the wool protein, while reduction followed by treatment with trimethylene dibromide maintains the molecular weight by rebuilding cross-linkages of a type that are extremely stable to alkali.

Susceptibility to degradation by alkali, which has been one of the most important practical disadvantages of wool, can now be overcome to a large extent through conversion of relatively unstable disulfide cross-linkages to extremely stable thioether cross-linkages. The stability of wools of this sort, under a variety of conditions of practical interest, is now being investigated in this laboratory.

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Photochemical Reactions in Silk

By HENRY A. RUTHERFORD AND MILTON HARRIS

A Textile Foundation Publication

Abstract

Silk is more readily deteriorated by the action of light than any other natural textile fiber. While the nature of the deterioration has not been clear, it has been known that the rate of decomposition may be considerably altered by pretreatment of the fiber with solutions of various chemical compounds. For example, silk treated with dilute solutions of basic compounds is more stable toward the action of light than untreated silk, whereas silk treated with dilute solutions of mineral acid exhibits greatly decreased stability under the same conditions.

An investigation by Research Associates of the Textile Foundation at the National Bureau of Standards of the influence of a number of reagents on the photochemical deterioration of silk now reveals that the rate of deterioration is in part influenced by the cationic content of the silk. The removal of cationic substances, by two independent methods results in practically identical decreases in the stability of the fibers to light. On the other hand, the stability is readily restored by treatment with basic compounds. Inorganic bases produce a number of undesirable effects, such as a harsh "feel" and a tendency for the cloth to yellow. These effects can be eliminated by the use of any one of a number of different organic basic compounds.

It was further shown that the inactivation of the carboxylic acid groups of silk by methylation with diazomethane does not appreciably change the photochemical behavior of the fiber but that the methylation of only a small percentage of the hydroxyl groups of tyrosine results in a marked increase in photochemical stability. The results suggest that alteration of the tyrosine hydroxyl groups by reaction with various reagents is responsible for at least part of these stabilizing effects.

I. Introduction

THE results of numerous investigations have indicated that silk is probably more readily deteriorated by light than any other natural textile fiber. While the mechanism of the decomposition is not clear, it appears that the rate of decomposition may be considerably altered by pretreatment of the fiber with various chemical reagents. For example, Harris and Jessup [1, 2] found that silk treated with dilute solutions of sodium hydroxide is more stable towards the action of light than untreated silk,

whereas the stability of silk treated with dilute solutions of sulfuric acid is greatly decreased. These findings were later substantiated by investigations by Hall.[3] Bonicatti,[4] on the other hand, claimed that pretreatment with alkalies has no protective effect but he did observe the photochemical decomposition to be greatly accelerated by treatment of the fiber with dilute solutions of mineral acids. More recently, Weilenmann [5] showed that some aliphatic and aromatic amines exhibit a protective action while compounds such as aliphatic amides and amino acids are not effective.

The efficacy of the basic compounds in inhibiting decomposition is of considerable interest, especially since it has recently been found by Gleysteen and Harris [6] that most of the base taken up by silk is bound by the hydroxyl groups of the amino acid tyrosine. It is now shown that the photochemical behavior of silk is associated with the behavior of the tyrosine and that alteration of the tyrosine hydroxyl groups by reaction with various reagents is responsible for at least part of the stabilizing effects noted in the past.

II. Experimental Procedure

1. Materials

The silk used in this work was a plain-woven cloth, commercially degummed, having 94 threads per inch. The cloth was first extracted with cold alcohol and with ether, and then washed in cold distilled water to remove the organic solvents. This silk is hereafter referred to as *degummed* silk.

The removal of cations from the silk was accomplished either by electrodialysis or by treatment with acid below pH 2.5. This material is hereafter referred to as *electrodialyzed* silk or *acid-treated* silk, according to the process by which it was prepared. Purification by electrodialysis has the advantage of eliminating possible secondary reactions which may be produced by treatment of the fibers with acidic solutions.

Methylated samples were prepared using diazomethane according to the procedure recently described by Rutherford, Patterson and Harris.[7] The acidic groups of degummed and of electrodialyzed silk have different rates of reaction with diazomethane, and it was possible to methylate an approximate, predetermined fraction of the carboxylic acid and tyrosine hydroxyl groups. The extent of methylation of each of these groups was directly determined by the procedure previously described.[7] The decrease in tyrosine content is a measure of the hydroxyl groups methylated. The difference between the total methoxyl content and the methoxyl content accounted for by the decrease in tyrosine content is a measure of the carboxyl groups esterified. Samples * I and II were treated for ¼ and for 1½ hours, respectively, in an ethereal solution of diazomethane but were not electrodialyzed or wet out with alcohol before the treatment; sample III was first soaked in 75-per cent alcohol, and then treated for ¼ hour with diazomethane. All of these samples were then electrodialyzed to remove cationic substances. Samples IV and V were electrodialyzed, wet with alcohol, and then treated for ¼ and for 16 hours, respectively, with diazomethane. With the exception of sample V, which lost about 15 per cent in strength, the methylation process had little effect on the strength of the fabric.

* See table 3.

2. Methods

The general procedure used in the preparation of the samples for irradiation was as follows: Pieces of the cloth were soaked for 30 minutes in a solution of a given reagent, the ratio of silk to solution being 1 to 100. The greater part of the solution was removed by centrifuging, the cloth being suspended on a wire rack in a centrifuge tube so that practically complete separation of the sample and solution was obtained. When the same piece of cloth was given one or more additional treatments, this same procedure was followed for each treatment. The silk cloth was finally air-dried and then cut into warpwise strips 1¼ inches wide which were then raveled down to 94 warp threads suitable for breaking strength tests. The samples were then exposed to the light for 20 hours. To determine the effect of light alone a second group of samples, treated and prepared in the same way, was kept for 20 hours in the dark under conditions of temperature and humidity approximating those encountered during the light exposure.

The decrease in breaking strength of the cloth was used as a measure of the deterioration of the silk. The tensile strengths were determined on a pendulum type machine, the samples being conditioned and tested in a room maintained at a temperature of 70° F. and a relative humidity of 65 per cent.

The source of light was the eveready accelerated testing unit, type C3A, equipped with Eveready Sunshine carbons and Corex D ultraviolet-transmitting glass. The exposures were made for 20 hours at a temperature of 55 to 60° C.*

The cationic contents of the various samples were determined quantitatively by the electrodialytic method of Sookne, Fugitt and Steinhardt.[8] Tyrosine was determined by Lugg's method after an alkaline hydrolysis,[9] and methoxyl content by the method of Vieböck and Brecker.[10]

III. Results and Discussion

1. The effect of removal of cations on the rate of deterioration

It was observed in preliminary experiments that pretreatment of the silk with practically any basic compound has the effect of reducing the rate of deterioration. This suggested the possibility that the increased stability produced by these substances might result from combination of cations with the acidic groups of the fibers, which are of two types, namely, carboxylic acid and tyrosine hydroxyl groups, and conversely, that the decreased stability observed upon treatment with dilute mineral acids might be due in part to removal of cationic substances from these groups. On the basis of these considerations, it appeared advisable to study the behavior of silk freed from these substances by electrodialysis and by treatment with acid.

The results are shown in table 1. Electrodialysis of the silk resulted in lowering the cation content from 0.13 to 0.01 milliequivalent per g and at the same time appreciably decreased the stability of the silk to light. Simi-

* This was measured by a mercury thermometer, the bulb of which was covered by a piece of the silk, and placed the same distance from the light as the samples.

Table 1. Effect of electrodialysis and of treatment with dilute acids on the deterioration of silk cloth.

Sample	Treatment	Cation content	Loss in breaking strength on exposure to light
		M. eq/gm	%
Degummed	None	0.13	32
Electrodialyzed	None	0.01	41
Degummed	H_2SO_4 (pH 2.4)	0.004	41
Degummed	H_2SO_4, followed by water wash	0.005	41
Degummed	HCl (pH 2.4)	0.002	43
Degummed	HCl, followed by water wash	0.002	43
Degummed	CH_3COOH (pH 2.4)	0.004	43
Degummed	CH_3COOH, followed by water wash	0.005	41
Electrodialyzed	H_2SO_4 (pH 2.4)	0.004	43

lar results were obtained when the samples were pretreated with solutions of hydrochloric, sulfuric or acetic acids at pH 2.4.* Thorough washing of the acid-treated samples with distilled water prior to exposure did not alter the stability to light, which indicates that the decrease in stability results from removal of cations and is not caused by the presence of free acid in the exposed samples. It was found that none of the silk samples kept in the dark exhibited any deterioration, showing that the deterioration of the irradiated silk was not thermal, but photochemical.

2. The effect of pretreatment with different cationic substances

During processing, such as dyeing, silk is frequently treated with acidic solutions which, as seen from the foregoing experiments, reduces the cation content and increases the susceptibility of the fiber to damage by light. The question whether the stability of acid-treated silk can be increased by replacement of cations thus becomes of importance.

Preliminary experiments showed that basic inorganic substances such as sodium hydroxide or sodium carbonate are effective for increasing the stability of the silk but they impart a harsh, undesirable feel to the cloth. It was observed, however, that basic organic compounds do not produce such undesirable effects and accordingly, a few of these types of compounds were studied. The effect of pretreatment of samples of degummed and electrodialyzed or acid-treated silk with 0.01 *M* solutions of several cationic compounds is shown in table 2. The data show that the deleterious effect, on light exposure, produced by acidic treatments can be reversed by treatments of the silk with suitable reagents. It is seen that the stability of the silk to light increases with increase in pH of the solutions used for

* The choice of this pH was based on the titration studies of Gleysteen and Harris[6] in which it was shown that removal of cations from silk becomes appreciable below about pH 3.

Table 2. Effect of different cationic substances on the deterioration of silk.

Sample	Treatment *	pH of solution	Loss in breaking strength on exposure to light
			%
Degummed	—	—	32
Acid-treated	—	—	41
Electrodialyzed	—	—	41
Degummed	dodecyltrimethylammonium bromide (Tech.)	6.0	32
Acid-treated	dodecyltrimethylammonium bromide (Tech.)	6.0	33
Degummed	dodecyltrimethylammonium bromide (Tech.)	9.8	24
Acid-treated	dodecyltrimethylammonium bromide (Tech.)	9.8	26
Degummed	triethanolamine	10.4	26
Acid-treated	triethanolamine	10.4	23
Electrodialyzed	triethanolamine	10.4	26
Degummed	trimethylbenzylammonium hydroxide	11.5	21
Acid-treated	trimethylbenzylammonium hydroxide	11.5	19
Electrodialyzed	trimethylbenzylammonium hydroxide	11.5	19
Degummed	dimethyldibenzylammonium hydroxide	11.5	21
Acid-treated	dimethyldibenzylammonium hydroxide	11.5	21
Electrodialyzed	dimethyldibenzylammonium hydroxide	11.5	21

* *The concentration of the solutions was 0.01 M. Treatment with more concentrated solutions gave no additional protection.*

treatment of the silk. This is to be expected, since as shown by the titration curve of silk,[6] the binding of cations also increases with increasing pH. In addition to pH, the chemical nature of the cationic substance may also influence the rate of the photochemical decomposition, but sufficient data are not available to enlarge upon this point.

In general, the inhibiting action of a given compound was independent of the history of a given sample; thus, degummed, acid-treated, or electrodialyzed silks all exhibited the same stability after treatment with a given reagent.

It was noted that the use of a cationic substance in the form of the salt, such as dodecyltrimethylammonium bromide (Tech.) had no effect on the degummed silk although it did raise the stability of the acid-treated sample to that of the degummed sample. Addition of enough dilute sodium hydroxide to raise the pH of the salt solution to 9.8 produced a significant increase in the stability of both, although an equivalent amount of sodium hydroxide alone had no measurable effect on the silk. The reason for this

is found in the titration studies of silk [6] in which it was shown that, at a given pH, silk combines with considerably more base in the presence of salts than in their absence.

When the samples, which had been treated with the reagents listed in table 2, were washed thoroughly with distilled water most of the inhibiting effects of the reagents were eliminated. The stabilities were lowered to about that of the original degummed silk, but they were still higher than those of the electrodialyzed or acid-treated samples. The pH of the water used for washing the samples was about 6.5 and accordingly, the silk would have still retained appreciable amounts of cations,[6] which would account for these differences. It may be that Bonicatti's [4] failure to observe the stabilizing effect of cations resulted from his use of degummed silk which might have contained appreciable amounts of cation. This appears likely since he found a marked decrease in the stability of his silk when he pretreated it with acid.

3. The effect of methylation

It is shown in the previous sections that the removal of cationic substances from silk by two independent methods results in practically identical decreases in stability to light, but that the stability can be restored by treatment with basic compounds. The question therefore arises whether the decreased stability obtained after electrodialysis or acid treatment is caused by the removal of cations from the carboxylic acid or the tyrosine hydroxyl groups, or from both.

It is not possible to ascertain by a simple experiment whether the cations are combined with carboxyl groups, tyrosine hydroxyl groups, or both. However, it is possible to inactivate known amounts of either type of group with diazomethane.[7] The results of such a procedure, applied to silk containing 0.002 milliequivalent, or less, of cation per gram, are shown in table 3. It was found that methylation of 5 per cent of the

Table 3. The effect of selectively methylating carboxyl and tyrosine hydroxyl groups with diazomethane on the deterioration of silk.

Sample	Carboxyl	Tyrosine hydroxyl	Loss in breaking strength on exposure to light
	percent of total	percent of total	%
Electrodialyzed	0.0	0.0	41
I	0	5	35
II	15	16	31
III	31	15	31
IV	67	17	32
V	100	87	23

hydroxyl groups produces a significant increase in the stability of the silk. Samples II, III, and IV were approximately equal with regard to the methylation of the hydroxyl groups and equal with regard to their stabili-

ties to light, although they differed greatly with respect to the extent of methylation of their carboxyl groups. This shows that the methylation of the latter has no effect on the stability of the silk. However, a further increase in the methylation of the hydroxyl groups, from 17 to 87 per cent of the total, produced still greater stability. The stabilities attained are comparable to the stabilities of those samples which were treated in alkaline solutions at pH 10.4 or above (table 2). Some additional evidence suggesting a confirmation of this explanation for an increase in the stability of silk on treatment in basic solutions was obtained in the following way. Portions of samples IV and V were treated with triethanolamine and trimethylbenzylammonium hydroxide and the treated samples were then irradiated for 20 hours. As shown in table 4, treatment of sample V had

Table 4. Effect of cationic substances on the deterioration of samples of silk methylated to different extents.

Sample	Treatment	Loss in breaking strength on exposure to light
		%
IV	None	32
IV	triethanolamine, pH 10.4	27
IV	trimethylbenzylammonium hydroxide, pH 11.5	18
V	None	22
V	triethanolamine, pH 10.4	25
V	trimethylbenzylammonium hydroxide, pH 11.5	22

little additional effect on stability. This was to be expected since most of the hydroxyl groups had already been methylated. On the other hand, the stability of IV after similar treatments was appreciably increased. In this sample, however, a large number of hydroxyl groups were still available for combination with the cations.

The increase in stability of silk, obtained by replacing the hydrogen of the hydroxyl group of tyrosine by methyl groups or by various cations, may result from a change in the absorption spectrum of the silk. The absorption spectra of some simple aromatic hydroxy-aldehydes and hydroxy-ketones are changed by similar treatments.[11]

4. Effect of the irradiation on the tyrosine content of silk

The deterioration of silk fibers by photochemical reactions probably results from a photochemical fragmentation of the polypeptide chains of the protein.[3] Some of the tyrosine may be destroyed [12, 13] and peptide linkages adjacent to the tyrosine cleaved.[14] Destruction of some of the tyrosine was also noted in the present investigation as shown by the data in table 5. It is of interest to note that the decrease in tyrosine content was accompanied by a corresponding decrease in tensile strength, and that treatments which tended to increase the stability of the silk decreased the amount of tyrosine destroyed.

Table 5. Photochemical decomposition of treated and untreated silk measured by change in tyrosine content and breaking strength.

Sample	Tyrosine	Loss in breaking strength on exposure to light
	%	%
Degummed (unexposed)	12.1	—
Degummed + triethanolamine (pH 10.4)	12.0	33
Degummed + sodium hydroxide (pH 10.7)	11.5	53
Degummed	11.1	62
Acid-treated	10.9	77

5. Practical significance

The above observations show that the stability of silk to light can be considerably increased by treatment with suitable cationic reagents. Experiments with several organic bases show that the undesirable effects produced by inorganic bases can be avoided by the use of proper organic reagents. In addition, the latter type of compounds appear to be more efficient in regard to stabilizing the silk. It should be noted that with the exception of the diazomethane treatment, none of the effects of the treatments used in this work was of a permanent nature, since the stabilizing effect was removed by washing the fabrics with water. It may be possible to develop colorless, basic compounds which might have sufficiently high affinities for the fiber so that they would resist removal by washing in neutral or alkaline solutions. Whether any of these treatments will affect other properties of the fabric such as light-fastness of the dye which may be used can only be determined for the materials to which such reagents may be applied.

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Donald Comer Reappointed a Director of Textile Foundation

THE REAPPOINTMENT by President Roosevelt of Donald Comer as a member of the Board of Directors of the TEXTILE FOUNDATION for a term of four years, has just been announced by the White House.

Mr. Comer, of Birmingham, Alabama, one of the country's leading cotton manufacturers, is distinguished not only as an industrialist, but also for his long record of public service as a private citizen. He is intimately associated with Alabama's fine record of social advances, and has always been in the forefront of movements to improve the position of the cotton textile industry as well as that of the workers and public associated with it.

Mr. Comer's reappointment is of particular significance at this time, in view of his warm enthusiasm for the Foundation's plan for the expansion of its activities, through closer association with the UNITED STATES INSTITUTE FOR TEXTILE RESEARCH. The new working arrangements are already in operation.

Abstracts

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I. Fibers (Synthetic and Natural) and Fiber Analysis

Powdered Wool: Composition. J. I. Routh. *J. Biol. Chem.*, 1940, V. 135, P. 175–181; abs. in *J. T. I.*, Oct. 1940, V. 31, P. A585.

The prolonged grinding of wool in a steel ball mill produced little change in the total nitrogen and sulphur content. The cystine content of the powdered material decreased appreciably. Aqueous extracts contained increased amounts of nitrogen, amino nitrogen, cystine, inorganic sulphates, and the intermediate oxidation products of cystine. The production of powdered wool was accompanied by oxidation, since the cystine sulphur accounted for a decreased percentage of the total sulphur and more than 50% of the water-soluble sulphur was in the form of inorganic sulphates. (C)

Ramie Fiber: Structure. G. Centola. *Atti X Congr. Intern. Chim.*, 1939, V. 4, P. 129–37; *C. A.*, 1940, V. 34, Col. 2169; abs. in *J. T. I.*, Sept. 1940, V. 31, P. A504.

From an investigation of the acetylation of native and mercerized ramie the following conclusions are drawn. (1) About 40% of the cellulose is amorphous and acetylates rapidly to the triacetate without altering the dimensions of the crystalline portion of the fiber. (2) Mercerization increases the content of amorphous cellulose. (3) The amorphous and crystalline portions are so intimately mixed that no deformation of the fiber is observed when partially acetylated ramie is extracted with solvents for cellulose acetate. (C)

RAW MATERIALS FOR NYLON. *Brit. Plastics,* August 1940, V. 12, P. 80; abs. in *Eastman Kodak Abs. Bull.,* November 1940, P. 590.

Although nylon is a generic name for resins formed by condensation between aliphatic dicarboxylic acids and aliphatic diamines, in practice, sebacic, adipic, and methyl adipic acids, on the one hand, and hexamethylenediamine and decamethylenediamine, on the other, are the only materials available at commercial prices. Adipic and methyl adipic acids are produced from phenol and cresol, respectively, by high-pressure catalytic hydrogenation followed by oxidation. Adipic acid can also be made from cyclohexene, which is available in quantity from suitable petroleum cuts. Sebacic acid is made from castor oil by fusion with caustic soda. The diamines can be made from adipic and sebacic acids by way of nitrile and high-pressure hydrogenation. Hexamethyldiamine can also be made from heptaldehyde, which is conveniently obtained from castor oil. (S)

THE RESIN FIBER "VINYON." F. Bonnet. *Am. Dye. Rptr.,* 1940, V. 29, No. 21, P. 547–8. (C)

SOYBEAN PROTEIN FIBERS: PRODUCTION. R. A. Boyer. *Ind. Eng. Chem.,* 1940, V. 32, P. 1549–1551; abs. in *J. T. I.,* March 1941, V. 32, P. A97.

The production of fiber from soybean protein is briefly described. When good protein is used, spinning solutions containing 20% protein can be obtained. The alkaline solutions are spun into precipitating baths containing sulphuric acid, formaldehyde and a salt such as sodium chloride or aluminum sulphate. The filaments are stretched between godet wheels, treated with a formaldehyde setting bath, cut to the desired staple length and dried under controlled humidity and temperature conditions. The strength of the fibers is about 80% of that of wool, but the extensibility is greater than that of wool in both the dry and wet states. Soybean fiber does not wet so easily as wool and casein fiber, and is more resistant to moulds than casein fiber. Recent refinements in processing have produced a soybean fiber which is highly resistant to carbonizing and to boiling in dilute acid and alkali. The fiber has a warm soft feel, a natural crimp and a high degree of resilience and it can be produced in natural color or can be spun dyed. It blends well with wool and cotton and has been processed satisfactorily on both cotton and worsted machinery. Plans are being made for a pilot plant capable of producing 1000 lb. of soybean fiber per day. (C)

STRETCHED ACETATE RAYON: MECHANICAL PROPERTIES. H. Lohmann. *Angew. Chem.,* 1940, V. 53, P. 107–9; *British Chem. Physiol. Abs.,* 1940, B, P. 729; abs. in *J. T. I.,* Jan. 1941, V. 32, P. A18.

With increasing degree of orientation, attained by soaking in 50% aqueous dioxan and stretching, the breaking strength of cellulose acetate rayon increases considerably, whilst the ultimate elongation, cracking, and knotting strengths decrease. Increased orientation increases the brittleness of the fiber, thereby impairing the transverse strength. An increase in the degree of polymerization increases the strength in both the longitudinal and transverse directions, and therefore for each degree of polymerization there is an optimum degree of orientation which leads to a suitable ratio of the strengths in the longitudinal and transverse directions. (C)

II. Yarns and Fabrics

The Reactivity of the Sulphur Linkage in Animal Fibers. V. Methods for Realizing a Permanent Set at Low Temperatures, with Observations on the Repair of Damage in Animal Fibers. J. B. Speakman, J. L. Stoves, and H. Bradbury.

In this new method of setting animal fibers at low temperatures, the fibers first are relaxed by treatment with a concentrated solution of sodium bisulphite in aqueous alcohol at 35° C. The washed fibers, if not already in the desired configuration, can then be deformed and treated with either (*a*) an alkaline oxidizing agent, e. g., an ammoniacal solution of potassium persulphate containing a swelling depressor, or (*b*) a solution of sodium tungstate or sodium aluminate, containing a swelling depressor.

It seems likely that the application of the above principles of linkage rebuilding to the lustring process will give yarns of sufficiently improved strength to make the process practicable. In general, the new methods of rebuilding linkages in bisulphite-treated fibers may be utilized to repair fiber damage caused, e. g., in bleaching with sodium bisulphite or in stripping dyed materials with sodium hydrosulphite. (C)

Silk Throwing and Its Relation to Dyeing and Finishing. George A. Urlaub. *Rayon Text. Mo.*, April 1941, V. 22, P. 63–4. (C)

Some Effects of Worsted Open Drawing on Fiber Length Distribution. Ronald Williamson. *J. T. I.*, Dec. 1940, V. 31, P. T235.

As a result of their passage through the operation of worsted open drawing, two qualities of wool have been noted to decrease in mean length. The decrease of the medium quality was small (3%) and was confined to the later processes, whilst the finer quality underwent a much greater decrease (17%), there being a substantial change with each operation.

Experiments made by increasing the draft and twist insertion each caused greater fiber breakage; approximately 50% more with the fine quality and 25% more with the medium quality. Increase of ratch did not appreciably affect the rates of fiber breakage. It was found that these changes of machine settings could only be made within narrow limits without impairing general processing efficiency. The changes were confined to these limits.

Changes in the recorded fiber lengths of the several slubbings and the rovings were noted to be due to:

(a) fiber breakage;

(b) elongation of the fibers through loss of crimp;

(c) the differential action of the fiber length tester according to the form in which the fibers entered the tester. Each of these has been investigated.

No increases of the actual fiber length, nor any changes in properties of extension, were to be noted.

The results of the tests have been expressed as the mean fiber length of each slubbing or roving, and a method of calculating the actual amount of fiber breakage has been given. (C)

III. Chemical and Other Processing (Not Otherwise Classified)

Making Cotton Fabrics Crease-Resistant. P. M. Pogozhef. *Khlopchatobumazhnaya Prom.*, 1937, No. 12, P. 30–4; *Chem. Zentr.*, 1939, I, Col. 2104; cf. *C. A.*, 1940, V. 34, Col. 4277; abs. in *C. A.*, V. 34, Col. 7615.

The artificial resins obtained from the condensation products of urea or of phenol and HCHO are well-suited for rendering cotton fabrics crease-resistant. They are colorless, completely transparent, elastic, stable and condense slowly so that their penetration into the fabric is facilitated, and they can be absorbed from water. On the basis of expts. reported, the following optimum conditions are given for the impregnation of cotton fabrics with the artificial resin formed from urea and HCHO: The mol. ratio of urea to HCHO should be 1:2 or 2:3. The production of a transparent and elastic film is assured by the addn. of HOAc or especially by the addn. of NH_4OAc. The condensate of urea and HCHO must consist of the products of the first stage of the condensation, i. e., of a mixt. of mono- and dimethylurea with a little methyleneurea. It is recommended that before impregnation with the resin the fabric be treated with alizarin oil or be mercerized (in the case of thin fabrics). The most satisfactory temp. for impregnation is 15–20°. The final condensation and fixation of the resin on the fabric is accomplished by heating to 165–70° for 2–3 min. After treatment, the fabric is washed with hot water at 50° and with soap at 60–5°. It is permissible to replace a part of the urea by thiourea or phenol. The presence of the resin does not interfere with the dyeing of the fabric to a fast color. The carrying out of the method on a plant scale is accurately described. (C)

Modern Methods of Controlling Old Dyehouse Hazards. Noel D. White. *Rayon Text. Mo.*, March 1941, V. 22, P. 91–2. (C)

A New Factor in Textile Chemistry. The Hydrogen Bond-Contributor to Fiber Structure and to the Dyeing of Textiles. Charles F. Goldthwait. *Am. Dye. Rptr.*, V. 30, No. 7, P. 166–68.

The hydrogen bond, or bridge, a rather new conception in chemistry is now believed to play an essential part in the structures of cellulose and of protein fibers, as well as in the fixation of dyes on fibers. The bonds are also effective in some dye solutions to hold dye molecules together in colloidal particles; and in other materials used on textiles, such as starch. Hence the hydrogen bond is apparently to take an important place in explaining some of the more fundamental and difficult problems in textiles. (C)

New Protective Lacquers for Dyeing Paddles, Drying Racks, etc. Hans Weise. *Mell. Textilber.*, V. 21, 184 (1940); abs. in *C. A.*, V. 34, Col. 5665.

Benzylcellulose lacquers and Resol, a cold-setting phenolic resin lacquer, are recommended to replace the presently used chlorinated rubber. (C)

AN OUTBREAK OF DERMATITIS FROM NEW RESIN FABRIC FINISHES. Louis Schwartz, Louis W. Spolyar, Frank U. Gastineau, John E. Dalton, Adolph B. Loveman, Marion B. Sulzberger, Ellis P. Cope and Rudolf L. Baer. *J. Am. Med. Assoc.*, V. 115, P. 906–11 (1940); abs. in *C. A.*, V. 34, Col. 8293.

A widespread outbreak of dermatitis was found to be due chiefly to the irritating effect of an acid ester gum used as a finish for different fabrics. Numerous important regulatory measures are recommended to prevent such recurrences. (C)

THE POSITIONAL INFLUENCE OF CHLORINE AND OF THE NITRO-GROUP ON THE COLORS OF CERTAIN AZO DYES. Colorimetric Evidence for the Mesomeric and Inductive Effects. H. H. Hodgson and E. Leigh. *J. Soc. Dyers Col.*, March 1941, V. 57, P. 82–6.

The reflection spectra of 51 dyes have been examined for light of 10 different wavelengths by means of the Bolton-Williams Colorimeter, over a wave-band of 680–440 mμ with the object of ascertaining the influence of nitro- and chloro-groups on their reflective (absorptive) powers. The dyes were used in the form of insoluble azo colors on cotton, and were obtained by diazotizing 17 amines and coupling them on the fiber with β-naphthol, Brenthol AS, and Brenthol BN, respectively. Colorimetric evidence was afforded in the first series of dyes with β-naphthol of the negative-inductive ($-I$) effects of the chlorine, of the nitro-group and of the second nucleus in naphthalene, of the positive ($+M$) mesomeric effect of chlorine, and of chelations which account for apparently paradoxical results. The results from the β-naphthol dyes were confirmed by the data of the analogous Brenthol compounds, although in these dyes the differences were not so marked as in the former dyes. It is assumed throughout in the electronic argument that since the dyes are *o*-hydroxy-azo compounds, their structures are entirely in the quinone-hydrazone form, and that the influence of the various effects is to be found in the degree of ionization of the imino-chromophore group. (C)

REPLACEMENT OF ACETIC ACID BY AMMONIUM SULFATE IN THE DYEING OF SILK WITH DIAZO DYES. Ya. K. Tyumenev. *Shelk*, V. 8, No. 5, P. 41 (1938); *Chem. Zentr.*, 1938, II, 2651; cf. *C. A.*, V. 33, Col. 5192; *Ibid.*, V. 34, Col. 6079.

In the dyeing of natural silk with blue and black diazo dyes the silk is treated with the dye soln. in the presence of Glauber salt at 30° for 30 min. after which $(NH_4)_2SO_4$ is added instead of HOAc. The bath is brought to boiling within 40–45 min., kept at this temp. 20 min., and then treated with steam for 15–20 min. (C)

"SHRINK-PROOFING" OF WOOL WITH BROMINE. Ralph L. Ericsson. *Am. Dye. Rptr.*, 1940, V. 30, No. 24, P. P641–P646. (C)

SURFACE ACTIVE AGENTS IN THE DEGUMMING OF SILK HOSIERY. O. M. Morgan and H. Seyferth. *Am. Dye. Rptr.*, 1940, V. 29, No. 23, P. P616–P622. (C)

TEXTILE STARCHES. Willard L. Morgan. *Am. Dye. Rptr.*, 1940, V. 29, No. 20, P. P494–P496. (C)

IV. Research Methods and Apparatus

Mercerized Cotton: Testing. L. Thompson. *Text. Recdr.*, 1940, V. 58, Nov., P. 37–41; Dec., P. 29–32; abs. in *J. T. I.*, March 1941, V. 32, P. A116.

The author reviews method for assessing the "efficiency of mercerization" by means of (*a*) shrinkage and luster, (*b*) deconvolution and swelling of the fiber, (*c*) moisture, dye and alkali absorption, and (*d*) chemical reactivity, and also discusses the changes in the cross-section of the cotton fiber and in the X-ray spectrogram of cellulose caused by swelling in caustic alkali. (C)

New Developments in the Ultramicroscope. P. Hatschek. *Phot. Ind.*, March 27, 1940, V. 38, No. 13, P. 213–14; abs. in *Eastman Kodak Abs. Bull.*, January 1941, P. 8.

A new type of electron microscope using electrostatic lenses instead of magnetic lenses has been developed by Brüche, Mahl, and Boersch, of the AEG Forschungsinstitut. In the instrument the same voltage is used on the electrostatic lenses as is used for accelerating the electron beam. This has the advantage that if the accelerating voltage fluctuates, the focussing voltages fluctuate with it, so that the image remains in focus. The power supply therefore need not be accurately regulated. The instrument can be operated with magnifications up to 6000. The resolving power is about 10 mμ. (S)

A New Electron Microscope. L. Marton. *Phys. Rev.*, 1940, V. 58, No. 1, P. 57–60; abs. in *Eastman Kodak Abs. Bull.*, January 1941, P. 8.

The design of a high-power electron microscope of the transmission type is described. It is constructed as a self-contained unit which may be operated by a practical microscopist who does not necessarily have training as a physicist. Photomicrographs are shown which indicate that a resolving power of about 50A. can be readily obtained. (S)

Polarizing Filters. E. Nähring. *Phot. Ind.*, Oct. 9, 23, 1940, V. 38, Nos. 41, 43, P. 599–601, 629–30; abs. in *Eastman Kodak Abs. Bull.*, Feb. 1941, P. 52.

One means of producing polarized light is available in certain dichroic crystals which break light into two polarized components, one of which is strongly absorbed. In 1852, Herapath found this effect with the material called "herapathite." Other organic dichroic crystals are quinine and pyridine derivatives. Two distinct kinds of polarizing filter are possible—one is a large, thin, dichroic crystal, and the second is the multiple-crystal form in which submicroscopic crystals are fixed in some matrix such as cellulose acetate. In this latter form, the crystals must be oriented by mechanical, electromagnetic, or electrostatic means while the matrix is viscous. The optical properties of the various kinds of dichroic materials are shown for both crossed and uncrossed sheet filters. Most materials show increasing transmission in the red and infrared. The multiple-crystal filter shows some light scatter. Other kinds of synthetic polarizing devices, such as the diffraction grating and reflecting types, are briefly mentioned. The methods of manufacture and use are discussed and

illustrated. Twenty-eight German, United States, and other patents are cited, together with a few literature references. (S)

POLYSTYRENE RESINS FOR MOUNTING. J. Kirkpatrick and A. C. Lendrum. *The Microscope*, September–October 1940, V. 4, No. 8, P. 210; abs. in *Eastman Kodak Abs. Bull.*, Feb. 1941, P. 69.

When a simple solution of polystyrene in xylol is used, there is marked retraction under the cover slip in a few weeks. This is eliminated by using a plasticizer, tricresyl phosphate. This is undoubtedly not the most stable possibility, dibutyl phthalate would probably be preferable. Unlike Canada balsam, the polystyrene is insoluble in a mixture of alcohol and xylol so that in the clearing of sections, the absolute alcohol must be replaced completely by xylol. Aniline dyes are preserved much better than with balsam. (S)

PREVENTION OF IMPERFECT SET MARKS. H. E. Wenrich. *Rayon Text. Mo.*, April 1941, V. 22, P. 77–8. (C)

RECENT ADVANCES IN TEXTILE TESTING METHODS. E. R. Schwarz. *Rayon Text. Mo.*, 1941, March, V. 22, P. 89–90. (C)

A SENSITIVE METHOD FOR THE DETERMINATION OF MOISTURE, APPLIED TO ELECTRICAL INSULATING MATERIALS. R. S. Vincent and A. Simons. *Proc. Phys. Soc.*, July 1940, V. 52, P. 489–500; abs. in *Eastman Kodak Abs. Bull.*, December 1940, P. 634.

A method is described for measuring the adsorbed moisture in paper samples, containing as little as 0.01 per cent moisture, in a total mass of as little as 0.1 gm. A description is given of a new form of absorption apparatus designed to measure the equilibrium water vapor pressure at a chosen temperature in a known space. This is found to be an excellent measure of the total adsorbed moisture. From several such measurements, each taking about two hours, the original total adsorbed moisture in the sample can be derived by graphical extrapolation. If the relation between equilibrium vapor pressure and percentage moisture is found for a particular type of material, a single vapor pressure measurement suffices to determine the total moisture content of a sample of the same material. (S)

THE SEPARATION OF VISCOSE AND COTTON BY SOLVENT ACTION. John H. Levin and Richard A. Martinell. *Text. Col.*, V. 62, P. 462–3 (1940); abs. in *C. A.*, V. 34, Col. 8290.

Viscose rayon dissolved completely when mixts. of cotton and viscose rayon were treated with Ca thiocyanate soln. (sp. gr. 1.36) at 87° for 25 min. The dissolved rayon was removed by washing with hot water. (C)

SIMPLIFIED PHOTOMICROGRAPHY. J. J. Rennick. *Photo Technique*, June 1940, V. 2, P. 60–1; abs. in *Eastman Kodak Abs. Bull.*, January 1941, P. 12.

A method for making photomicrographs, using a microscope, an enlarging stand, and a Rolleiflex camera, is described. The camera is attached to the enlarger support arm, from which the enlarger has been removed. The microscope is placed below the camera shutter so that, after

examining the specimen through the microscope eyepiece, the camera may be lowered into the operating position. Suggestions for exposure and illumination are also given. (S)

TEST FOR RESIDUAL CHLORINE. F. J. Hallinan. *Ind. Eng. Chem.; Anal. Ed.*, 1940, V. 12, P. 452–53; abs. in *J. Soc. Dyers Col.*, Dec. 1940, V. 56, P. 531.

Residual chlorine in highly colored wastes can be estimated by taking advantage of the adsorption compound formed on the colloidal indicator when potassium iodide and α-naphthoflavone are added. The chlorine-containing solution (50 ml.) is treated with a dry mixture of potassium iodide and buffer. (Generally, 20 g. potassium iodide and 20 g. sodium potassium tartrate per l. are used, giving a solution of *pH* 6.7.) The salts are dissolved rapidly and, after 2 min., 0.5 ml. of 0.2% α-naphthoflavone solution in 95% ethyl alcohol is added. After 3 min., the adsorption compound is coagulated by violent agitation and immediately collected in a Gooch crucible. Excess of indicator must be used. The precipitate is washed with about 2 ml. chlorine-free water, and the filtrate and washings discarded. The iodine is dissolved in 5 ml. 0.1% alcoholic potassium iodide solution, and the yellow filtrate then compared with permanent color standards prepared from inorganic solutions. (C)

TESTING FABRICS FOR SHRINKAGE. W. A. Dutton. *Hosiery Tr. J.*, 1941, V. 48, No. 565, P. 22, 24–5; No. 566, P. 28, 30, 32; abs. in *J. T. I.*, March 1941, V. 32, P. A121.

A fuller report of a lecture already noted (this *J.*, 1940, A677). Shrinkage by relaxation of stretch and manufacturing strains and by felting is discussed, and methods of testing these two types of shrinkage are described. Tests for controlling evenness of chlorination are also described, including those developed for "Warnorm" fabrics. (C)

TESTING THE U. S. SOLDIER'S UNIFORM. *Text. Age*, March 1941, V. 5, P. 48–51. (C)

ULTRAVIOLET AND ELECTRON MICROSCOPY. L. C. Martin. *Nature*, Aug. 31, 1940, V. 146, P. 288–92; abs. in *Eastman Kodak Abs. Bull.*, Feb. 1941, P. 61.

By decreasing the wave length of the radiation, the ultimate limit of resolution in conventional microscopy can be reduced to 10^{-5} cm. This limit can be reduced still further, using a perfectly homogeneous electron beam, which is a monochromatic radiation of shorter wave length (10^{-9} cm. for 15 kv. electrons), and which may be focussed by means of electric or magnetic fields. Spherical aberration in electron optical systems may not be entirely removed, and, if the aperture is cut down to reduce the effects of the residual aberration, the image will suffer because of the loss in intensity and the effects of diffraction. Calculations show that the resolution limit set by spherical aberration should be 10^{-7} cm. or 10^{-8} cm., but there are other limiting factors which are not yet widely appreciated. Lack of symmetry in the magnetic fields is analogous to bad centering in optical systems, and is difficult to rectify, but recent work on electrostatic focusing avoids this difficulty. (S)

THE USE OF THE BLACK CARPET BEETLE IN THE TESTING OF MOTHPROOFED MATERIALS. **Ruth E. Slabaugh.** *Am. Dye. Rptr.*, 1941, V. 30, No. 6, P. P142–46. (C)

V. PURE SCIENCE, ECONOMICS AND MISC.

MACROMOLECULAR COMPOUNDS: POLYESTERS. H. Staudinger and H. Schmidt. *J. prakt. Chem.*, 1940, V. 155, No. 6/7, P. 129–62; abs. in *Eastman Kodak Abs. Bull.*, November 1940, P. 584.

The molecular weights of various polyesters prepared from sebacic acid and hexanediol were determined by osmotic, viscometric, cryoscopic, and end-group methods. Products having molecular weights under 5,000 gave the same value by all of the above methods. However, the different methods gave quite discordant values for the super polyesters having molecular weights in the neighborhood of 10,000. One product gave a molecular weight of 14,400 by viscosity, 20,700 by osmotic pressure, and 4,850 by end-group determination. The authors believe that this behavior may be caused by the branching of the molecules and a possible reaction mechanism is indicated. A three-dimensional insoluble product was prepared from dimethyl sebacate and hexanediol. (S)

THE MECHANISM OF THE POLYMERIZATION OF VINYL ACETATES AND METHYL VINYL KETONE. H. W. Melville, T. T. Jones, and R. F. Tuckett. *Chemistry and Industry*, April 20, 1940, V. 59, No. 16, P. 267–72; abs. in *Eastman Kodak Abs. Bull.*, November 1940, P. 584.

A preliminary paper comparing the modes of polymerization in vinyl acetate and methyl vinyl ketone systems is given. Both systems appear to polymerize by a combination of double-bond and free-radical modes. In the case of methyl vinyl ketone, the latter mode leads to the formation of bifunctional radicals with subsequent cross-polymerization or cross-linkage. (S)

THE SEDIMENTATION OF SUSPENSIONS. L. T. Work and A. S. Kohler. *Trans. Amer. Inst. Chem. Engineers*, Oct. 25, 1940, V. 36, No. 5, P. 701–19; abs. in *Eastman Kodak Abs. Bull.*, Feb. 1941, P. 64.

Sedimentation of calcium carbonate and basic aluminum sulfate sludges was carried out in which long columns of the suspensions were slowly stirred during settling. The effects of the height of the columns and the concentration of the particles were correlated. A Stokes-law settling velocity occurs as a unit solid fraction is approached. The upward displacement of liquid is also considered with respect to the form of the curves obtained from the data. The apparatus is described. (S)

STARCH: MOLECULAR STRUCTURE. K. Freudenberg and H. Boppel. *Naturwissenschaften*, 1940, V. 28, P. 264; *C. A.*, 1940, V. 34, Col. 6232; abs. in *J. T. I.*, Dec. 1940, V. 31, P. A686.

The hydrolysis of completely methylated potato starch furnishes 2: 3: 6-trimethylglucose, a few per cent of dimethylglucose and a smaller amount of 2: 3: 4: 6-tetramethylglucose. The dimethylglucose appears to be a mixture of the 2: 6- and 2: 3-isomerides, the latter coming directly from the

methylated starch and the former from the trimethylglucose during the hydrolysis. The inference is drawn that branching of the chain in starch occurs on the 6-hydroxyl group. (C)

A Summary of the Reactions of Aldehydes with Amines. M. M. Sprung. *Chem. Reviews*, June 1940, V. 26, P. 297–338; abs. in *Eastman Kodak Abs. Bull.*, March 1941, P. 116.

A review is given dealing principally with the special reactions occurring between various types of aldehydes and amines. In general, aldehydes react with primary and secondary amines by simple addition ($R-CHO + H_2N-R' \rightarrow R-CHOH-NH-R'$); this product may, depending on conditions and on the reactants involved, dehydrate to form an imine (Schiff base). With aldehyde-amine systems, however, the above products, if present at all, are transitory since they may react with each other or with the reactants to form complex compounds. Among the special products formed from relatively simple aldehydes and amines (including ammonia) are: hexamethylene tetramine, substituted pyridines, pyrimidines, imidazoles, di- and tetrahydroimidazoles, acridines, and quinolines. Almost all aldehyde-amine systems will react to form resins under certain conditions. Only a few have shown any promise commercially. The review contains 162 references. (S)

A Theory of Capillary Condensation in the Pores of Sorbents and of Other Capillary Phenomena, Taking into Account the Disjoining Action of Polymolecular Liquid Films. B. Derjaguin. *Acta Physicochimica U. R. S. S.*, 1940, V. 12, No. 2, P. 181–200; abs. in *Eastman Kodak Abs. Bull.*, March 1941, P. 112.

A generalization of Kelvin's equation for the lowering of the vapor pressure over a concave meniscus is derived which takes account of the effect of the water adsorbed on the walls of the capillaries. The necessary corrections in the calculations of other capillary phenomena are also given. (S)

Versatile Photomicrographic Unit. F. W. Bishop and V. Downing. *Photo Technique*, August 1940, V. 2, P. 48–50; abs. in *Eastman Kodak Abs. Bull.*, December 1940, P. 622.

The construction of a photomicrographic unit and its application to still and motion pictures are described. (S)

Water-saturated Surfaces: Evaporation from—. R. W. Powell. *Engineering*, 1940, V. 150, P. 238–39, 278–280. (C)

X-ray Investigations of Carbohydrates. H. Mark. *Chem. Reviews*, April 1940, V. 26, P. 169–86; abs. in *Eastman Kodak Abs. Bull.*, August 1940, P. 443.

The structural data on the simple carbohydrates is correlated with the known evidence on the cellulose structure. The copious literature on the cellulose lattice is reviewed and a compromise between a chain and layer lattice is postulated. (S)